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UNIVERSITY OF CONNECTICUT
Ternary Compounds NR-052-268
Contract No. ONR-367(00)
Third Technical Report
for the period
June 1, 1953 to May 31, 1954

UNIVERSITY OF CONNECTICUT

DEPARTMENT OF CHEMISTRY

TERNARY COMPOUNDS NR-052-268

CONTRACT NO. ONR-367(00)

THIRD TECHNICAL REPORT

for the period

June 1, 1953 to May 31, 1954

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I General Study of Perowskite Type Compounds

In view of the fact that many ternary oxides of the formula-type ABO_3 and the perowskite structure are now known, an attempt has been made to find some general relationships among them.

The ideal perowskite structure is cubic, with an A-cation, twelve-coordinated to oxygen, at the body center of the cube; B-cations, six-coordinated to oxygen, at the cube corners; and oxygens in the edge-centers. Both geometrical factors, as described in the Goldschmidt[1] equation, and valences must be satisfied in order for this structure to exist.

To obtain products with the ideal perowskite formula, ABO_3, if A = an alkaline earth cation, the transition metal should be tetravalent, and, if A = lanthanum, the transition metal should be trivalent. This necessitates unusual valence states for several of the transition elements. That these unusual valence states exist has been shown beyond doubt, but they are frequently not fully attained, so that variable valency, oxygen or A-cation deficiency, and peculiar conductance phenomena are found in many of the products. In the alkaline earth series, the deficiencies found so far, with the possible exception of strontium-vanadium and strontium-iron-oxides[2], have been oxygen deficiencies. The syntheses of the barium, strontium, calcium, and lanthanum oxides of the first period transition metals from vanadium to copper has been tried to complete this series of compounds.

Table 1 shows the alkaline earth and lanthanum series in which products have been obtained. Since the degree of oxygen deficiency seems to be dependent on the temperature and duration of heating, and, possibly, in some cases, on the reactants used, these data are included for the materials prepared (not necessarily originally) in this laboratory. Ideal formulae are used except where others have been established.

Table 1

Products Containing Alkaline Earth or Lenthanum, a First Period Transition Metal, and Oxygen

Product	Reactants	Color	Temperature	Atmosphere	Structure
$BaTiO_3(3)$		White	$<-90°C$	air	H
			$>-90°C, <-5°C$		O
			$>-5°, <120°C$		T
			$>120°C$		C
$BaVO_3?$	$Ba(NO_3)_2 + V_2O_3$	Black	$1000°C$	H_2	?
$BaCrO_3?$	$BaCrO_4$	Brown	$1050°C$	H_2	?
$BaCrO_3?$	$BaCrO_4$	Black	$1600°C$	air	?
$BaMnO_3$	$BaCO_3 + MnO_2$	Black	$900°, 1000°C$	air	DP
$Ba_8Fe_8O_{22}(4)$		Black	$800°C$	air	LP
$BaFeO_{2.72}$	$Ba(NO_3)_2 + Fe(NO_3)_3 \cdot 9H_2O$	Black	$700°C$	air	DP
$BaFeO_3?$	$Ba(NO_3)_2 + Fe(NO_3)_3 \cdot 9H_2O$	Amber	$1200°C$	air	?
$BaCoO_{2.72}(5)$		Black	$650°C$	air	P
$BaCoO_{2.86}$	$Ba(NO_3)_2 + Co(NO_3)_2 \cdot 6H_2O$	Black	$700°C$	air	DP
$BaCoO_{2.31}(5)$		Black	$900°C$	air	?
$BaCoO_{2.23}(5)$		Black	$1300°C$	air	P
$BaCoO_3$	$Ba(NO_3)_2 + Co(NO_3)_2 \cdot 6H_2O$	Black	$1200°C$	air	DP
$BaNiO_3(6)$		Black	$700°C$	O_2	H
$BaNiO_{2.48}$	$Ba(NO_3)_2 + Ni(NO_3)_2 \cdot 6H_2O$	Black	$700°C$	air	DP
$BaNiO_3$	$Ba(NO_3)_2 + Ni(NO_3)_2 \cdot 6H_2O$	Black	$900°C$	air	?
$BaNiO_3$	$Ba(NO_3)_2 + Ni(NO_3)_2 \cdot 6H_2O$	Decomposed	$<1200°C$	air	?
$BaCuO_3?$	$Ba(NO_3)_2 + Cu(NO_3)_2 \cdot 3H_2O$	I	$700-900°C$	air	?
$SrTiO_3(7)$					P
$SrCrO_3?$	$(NO_3)_2 + Cr_2O_3$	Yellow-green	$670°C$	air	M
$SrCrO_3?$	$SrCrO_4$	Dark green or black	$1200°C$	air or vacuum	?

Note: Key follows table.

Table 1 (continued)

Product	Reactants	Color	Temperature	Atmosphere	Structure
SrMnO$_3$(8)	Sr(NO$_3$)$_2$+MnO$_2$	Black	1000°C	air	?
SrFeO$_3$	Sr(NO$_3$)$_2$+Fe(NO$_3$)$_3$.9H$_2$O	Black	700°,900°,1100°C	air	DP
SrFeO$_3$	Sr(NO$_3$)$_2$+Fe$_2$O$_3$	Black	650°,900°,1200°C	air	DP
SrFeO$_3$?	Sr(NO$_3$)$_2$+Fe$_2$O$_3$	Liver-colored	1260°C	air	?
SrFeO$_3$	SrCO$_3$+Fe$_2$O$_3$	I	1200°C	air	DP
SrCoO$_3$	Sr(NO$_3$)$_2$+CoCO$_3$	Black	900°C	air	?
SrCoO$_3$	Sr(NO$_3$)$_2$+Co(NO$_3$)$_2$.6H$_2$O	Black	690°,700°,900°, 1000°C	air	?
SrNiO$_3$	Sr(NO$_3$)$_2$+Ni(NO$_3$)$_2$.6H$_2$O	Black	690°,700°,900°, 1000°C	air	?
SrNiO$_3$	SrCO$_3$+NiCO$_3$	Black	820°,900°,1260°C	air	?
SrCuO$_3$?	Sr(NO$_3$)$_2$.3H$_2$O+Cu(NO$_3$)$_2$.3H$_2$O	I	900°C	air	?
CaTiO$_3$(9)					DP
CaVO$_3$(10)					P
CaCrO$_3$?	CaCrO$_4$	Dark green or black	1100°,1200°C	air, vacuum	?
CaMnO$_3$(8)	Ca(NO$_3$)$_2$.4H$_2$O+MnO$_2$	Black	1000°C	air	P
CaCoO$_3$?	Ca(NO$_3$)$_2$.4H$_2$O+CoCO$_3$	Black	500°-900°C	air	M
CaNiO$_3$?	Ca(NO$_3$)$_2$.4H$_2$O+Ni(NO$_3$)$_2$.6H$_2$O	I	550°C	air	M
CaNiO$_3$?	CaCO$_3$+Ni(NO$_3$)$_2$.6H$_2$O	I	900°C	air	M
LaTiO$_3$(11)	La$_2$O$_3$+Ti$_2$O$_3$	Black	1200°C	vacuum	P
LaVO$_3$(12)	La$_2$O$_3$+V$_2$O$_3$	Black	1200°C	vacuum	P?
LaCrO$_3$(9)		Green	900°C	air	DP or P
LaMnO$_3$(8)	La$_2$O$_3$+Mn(NO$_3$)$_2$	Black	900°C	air	P
LaFeO$_3$(9)	La(NO$_3$)$_3$.6H$_2$O+Fe(NO$_3$)$_3$.9H$_2$O	Yellow-brown	900°C	air	LP or P
LaCoO$_3$(13)	La(NO$_3$)$_3$.6H$_2$O+Co(NO$_3$)$_2$.6H$_2$O	Black	900°C	air	R
LaNiO$_3$	La(NO$_3$)$_3$.6H$_2$O+Ni(NO$_3$)$_2$.6H$_2$O	Black	900°C	air	DP

Table 1 (continued)
Key to Table 1

H = hexagonal deformation of perowskite-structure

O = orthorhombic deformation of perowskite-structure

T = tetragonal deformation of perowskite-structure

R = rhombohedral deformation of perowskite-structure

? = uncertain

P = essentially simple perowskite

DP = deformed perowskite

LP = multiple-celled perowskite

I = inhomogenous product

I. 1 The Barium Series

Earlier work, done on this project and elsewhere, (8),(4),(5),(6) has shown
the existence of ternary oxides, of the type ABO_3, in the systems barium-manganese-
oxygen, barium-iron-oxygen, barium-cobalt-oxygen, and barium-nickel-oxygen. These
are perowskite-like or pseudo-perowskite-like phases. With the possible exception
of the manganese member, which has not yet been analyzed, they all exhibit oxygen-
deficient lattices. In no case save that of nickel(6) has the ideal formula
been observed.

Reactions have taken place, also, when attempts were made to produce $BaVO_3$
and $BaCrO_3$, but the products are not recognizable as perowskite-like or near
perowskite-like. There seems to be no geometrical reason for this, so it is
possible that, if proper conditions could be found, these two compounds might be
made.

Single crystals, of hexagonal habit, have been obtained for the low-temperature
iron, cobalt, and nickel members, and single crystal x-ray analysis is in process
on the barium iron oxide.

I. 2. The Strontium Series

The systems under consideration in this series are strontium-manganese-oxygen,
strontium-iron-oxygen, strontium-cobalt-oxygen, strontium-nickel-oxygen, and
strontium-copper-oxygen. They were prepared in the same way as the members of
the barium series, by heating mixtures of carbonates, nitrates, or oxides of
the desired A- and B-cations in such proportions as to give an A to B ratio of
one. Table 2 contains x-ray diffraction data for several of the products. No
homogeneous products were obtained with copper.

The strontium-iron phases are simplest, and have deformed perowskite-like
structures, as shown in Table VIII, page 13, in our Eleventh Quarterly Report.
In this system the fact has been noted that, if strontium carbonate and ferric
oxide be used as reactants, the degree of departure from cubic symmetry is much
less than if nitrates be used as starting materials (Table 3). This may be

caused by a greater oxygen deficiency in the former case, where the reactants themselves are less strong oxidizing agents than the nitrates. Study of reactions in a pressure-controlled oxygen bomb might resolve this problem.

The manganese, cobalt, and nickel phases are quite similar to each other in structure, and bear some resemblance to the iron phase, but are considerably more complicated. The strong lines of cobaltous oxide and nickel oxide can be found in the appropriate diffraction patterns. The iron, cobalt, and nickel products show qualitative evidence of valences greater than three, two, and two, respectively.

Valence determinations by the method of Struthers[14] give formulae $SrNiO_{2.24}$ for the product obtained by the reaction of nitrates at 700°C and $SrNiO_{2.16}$ for that obtained at 1000°C. This is in line with the valence decrease with temperature found in the barium-cobalt-oxygen[5] and barium-nickel-oxygen[6] systems.

Table 3 contains x-ray data for the strontium-iron-oxygen phases prepared from nitrates at 700°C, 900°C, 1000°C, 1100°C and in the range 1150-1260°C, and also for phases made at 900°C and 1200°C starting with strontium carbonate and ferric oxide.

The product prepared in the range 1150-1260°C is a ruby-red to amber-colored material, apparently formed from a melt. It shows hexagonal asterism, and is highly magnetic. In these respects it parallels the barium-iron-oxygen product made at temperatures above 1160°C. In both cases, the x-ray powder diffraction patterns were very poor.

Comparison of the data for strontium iron oxide with those for the lanthanum series, in particular $LaNiO_3$, in Table 4, shows that the strontium-iron phases have a much closer structural resemblance to the lanthanum transition metal oxides than to the other members of the strontium-transition metal-oxygen series.

Table 2

A Comparison of the X-ray Diffraction Data of the Strontium-Transition Metal-Oxygen Series

SrMnO$_x$ 1000°C		SrFeO$_x$ 900°C		SrCoO$_x$ 800°C		SrNiO$_x$ 800°C	
I	d/n	I	d/n	I	d/n	I	d/n
				w	6.24	w-	6.21
		w+	5.12			w--	5.81
				w+	4.77	w	4.75
				w--	4.55	w-	4.57
		w+	3.81	w--	3.65	w-	3.66
m-	3.29	w+	3.37	w-	3.37	w-	3.37
w+	3.12	w+	3.09	s-	3.12		
m	2.94	w	3.05	s-	3.05	s-	3.06
		s+	2.81	w--	2.83	w-	2.83
s	2.75	s	2.74	s	2.75	s	2.75
w+	2.58			w	2.46	w--	2.48
				w	2.37	m	2.42
w-	2.29	w+	2.32	w-	2.29	w-	2.29
w-	2.21	w-	2.24	w	2.22	w-	2.23
m	2.101	m	2.13	w+	2.13	w+	2.18
s	2.060			s-	2.053	m+	2.090
						m+	2.037
		m-	2.016			w+	1.980
w-	1.993	s-	1.933	m-	1.945		
m	1.862			w	1.893		
w-	1.773			w	1.815	w	1.822
w	1.682	w	1.685	w	1.683	w-	1.704
w	1.650	w	1.660	m	1.642		
w	1.619	m	1.623	w+	1.615	m	1.634

Table 2 (continued)

SrMnO$_x$ 1000°C		SrFeO$_x$ 900°C		SrCoO$_x$ 800°C		SrNiO$_x$ 800°C	
I	d/n	I	d/n	I	d/n	I	d/n
		m+	1.591	m	1.583	m-	1.579
w+	1.577	m+	1.583	w-	1.557		
w+	1.540	w--	1.542	w--	1.527	w--	1.518
w--	1.501	w	1.485	m-	1.504	m	1.477
w-	1.442	w-	1.437			w--	1.380
w--	1.409	m-	1.396	m	1.371	w++	1.368
w	1.380						
m-	1.365	m-	1.366	w	1.320		
w	1.277	w+	1.270	w-	1.277	w+	1.260
				m-	1.253	w	1.246
		m--	1.224	w-	1.193	w+	1.207
				w--	1.169		
		w+	1.148	w+	1.141	w+	1.134
		m-	1.132	w	1.091		
		w	1.059	w-	1.064		
		w	1.046	w-	1.052	w	1.049
		m--	1.036	w+	1.037	w-	1.039
		w	0.990	w	0.950	w	0.957
		w+	0.979				

Table 3
Effect of Temperature and Reactants on Structure in the System Strontium-Iron-Oxygen

700°C		900°C		SrCO₃ Fe₂O₃ 900°C		1000°C		1100°C		SrCO₂ Fe₂O₃ 1200°C		1150-1260°C	
I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n
		w+	5.12										
w	3.84			w	3.87					w-	3.93		
		w+	3.81					w	3.82				
								w-	3.53			w	3.70
w	3.38	w+	3.37			w-	3.37	w	3.38				
												w--	3.24
								w	3.13				
		(β of 2.81) w+	3.09										
		(β of 2.74) w	3.05			w	3.04						
												m	2.96
s	2.79	s+	2.81	w	2.79	s	2.79	s+	2.81			s	2.79
s	2.73	s	2.74	s	2.74	s	2.73	s+	2.74	s	2.75		
						w	2.63					m	2.63
						w-	2.52					w+	2.53
												m	2.43
						w-	2.40						
												w	2.37
w-	2.32	w+	2.32			w	2.30						
w-	2.22	w-	2.24	m	2.23	m-	2.23	w-	2.23	w+	2.24	w+	2.22
w+	2.12	m	2.13			s-	2.12	m	2.14			w+	2.14
												w+	2.031
								m-	2.020				
		m-	2.016										
w	2.013												

Table 3 (continued)

700°C		900°C		SrCO$_3$ Fe$_2$O$_3$ 900°C		1000°C		1100°C		SrCO$_3$ Fe$_2$O$_3$ 1260°C		1150-1260°C	
I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n
						m-	2.010						
												w-	1.957
		s-	1.933	m+	1.933	s	1.933	s	1.936	m	1.936		
m+	1.924												
												w-	1.915
						w--	1.752						
										w--	1.729		
w-	1.682	w	1.685					w	1.680				
		w	1.660			w-	1.669	w-	1.662			m-	1.664
						w-	1.653						
w	1.617	m-	1.623			m-	1.617	m-	1.625			m	1.625
												w	1.602
		m+	1.591					s-	1.594				
m	1.579	m+	1.583	m+	1.579					m+	1.579		
		w--	1.542										
		w	1.485					w-	1.486				
						w	1.477					m	1.472
		w-	1.437			w-	1.430	w	1.435				
w	1.395	m-	1.396			m-	1.390	m	1.393			w+	1.386
m-	1.362	m-	1.366	m	1.366	m+	1.364	m	1.368	m	1.369		
												m-	1.300
w	1.268	w+	1.270			w+	1.265	?w-	?1.263				
m	1.221	m--	1.224	m-	1.222	m-	1.221	m	1.225	w+	1.226		
				w-	1.164					w-	1.167		
w-	1.146	w+	1.148			w	1.146	w	1.148				
w	1.130	m-	1.132			m--	1.129	w+	1.133				

Table 3 (continued)

700°C		900°C		SrCO₃ Fe₂O₃ 900°C		1000°C		1100°C		SrCO₃ Fe₂O₃ 1200°C		1150-1260°	
I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n
w-	1.111			w+	1.116	w	1.113			w	1.117		
												w	1.102
												w	1.062
		w	1.059			w	1.058	w	1.062				
		w	1.046			w+	1.043	w	1.047				
w+	1.032	m--	1.036	m-	1.033	m-	1.032	w+	1.037	w+	1.034		
w-	0.991	w	0.990			w	0.987	w	0.990				
w-	0.977	w+	0.979			w+	0.976	w+	0.979				
		w+	0.967	w-	0.966	w+	0.964	w	0.967	w--	0.966		
		w-	0.927			w	0.926	w-	0.929				
w+	0.908	w+	0.912	w+	0.911	m-	0.911	m-	0.913	w+	0.910		
				w-	0.886					w--	0.887		
		w+	0.878			w	0.877	w	0.878	w	0.884		
		w+	0.871			w	0.870	w	0.872				
w+	0.862	w+	0.864	w+	0.865	m-	0.863	w+	0.864				
				w+	0.863					w--?	0.843		
		w	0.836			w	0.836	w-	0.836				
		w	0.828			w	0.827	w	0.828	w--	0.825		
				w	0.823					w--	0.822		
		m-	0.793	w	0.789	m-	0.794	w+	0.795	w	0.789		
										w	0.787		

Table 4

X-ray Powder Diffraction Data Showing Similarity in Structure of LaCoO$_3$(13) and LaNiO$_3$

Cubic Indexing		LaCoO$_3$(13)		LaNiO$_3$	
h k l	$h^2 + k^2 + l^2$	I	d/n	I	d/n
100	1	m	3.82	w+	3.86
110	2	vs	2.721	s+	2.73
		vs	2.681		
111	3	m	2.213	w	2.23
		w	2.178	w--	2.19
200	4	s	1.911	m	1.921
210	5	vvw	1.719	w	1.716
		vvw	1.701		
211	6	s	1.568	m	1.579
		m	1.545	w-	1.552
		m	1.360	w+	1.365
220	8	m	1.343	w	1.351
300, 221	9	vvw	1.275	v-	1.280
310	10	m	1.213	w	1.215
		m	1.204		
311	11	vw	1.154	w+	1.158
		vw	1.143		
222	12	w	1.108	w-	1.112
		vw	1.091		
320	13	vvw	1.068		
		vvw	1.055		
321	14	m	1.027	w+	1.029
		w	1.021		
		w	1.013	w-	1.016
400	16	w	0.956	w-	0.959

*LaCoO3(13) has been better indexed as rhombohedral, with an interaxial angle of 90°42'.

It has been suggested by W. Rüdorff and B. Reuter(2) that a strontium iron oxide with an x-ray diffraction pattern very much like those produced here has the formula $Sr_{0.67}Fe_{1.33}O_{2.67}$, and contains one fourth of its iron in the positions usually assigned to the A-cation. Such a formula, however, would imply that all of the iron is trivalent, whereas the oxide made in this laboratory has been shown to contain some iron in a higher oxidation state.

As in the case of strontium iron oxide, the main x-ray diffraction lines do not vary greatly for products obtained at various temperatures in the strontium-cobalt and strontium-manganese series. This is not true of the data for the strontium-nickel-oxygen system, but the nickel-containing products in this system are less stable than the others with respect to time and to increase in temperature of preparation.

I. 3 The Calcium Series

No further work has been done on this series in the current quarter. As indicated in our Eleventh Quarterly Report, Table XIV, page 20, a substance of probable formula $CaMnO_3$ exists, and is apparently a simple perowskite. X-ray diffraction by this material causes much darkening of the film, which may possibly have obscured any fine-line structure.

$CaVO_3(10)$ has been reported as simple cubic.

No phase of composition approximating the formula $CaFeO_3$ has been obtained, and no evidence has been found for the existence of a calcium-iron-oxygen compound in which iron attains a valence greater than three.

In the cases of cobalt and nickel, products have been obtained which liberate chlorine readily from dilute hydrochloric acid, indicating that the valences of the transition metals are in excess of two, but homogeneous phases have not been prepared, and the products are too reactive to be washed free of contaminants, even with dilute acetic acid.

I. 4 The Lanthanum Series

Prior to this report, the compounds $LaTiO_3$(11), $LaVO_3$(12), $LaCrO_3$(9), $LaMnO_3$(8) $LaFeO_3$(9,16), and $LaCoO_3$(13) had been reported. A detailed summary of the study of $LaTiO_3$ appears at the end of this section of the report.

Attempts in this laboratory to prepare $LaNiO_3$ had hitherto yielded products highly contaminated with lanthanum oxide. (This difficulty was also encountered in the preparation of $LaCoO_3$(13)). It has been found, however, that if the contaminated product be washed quickly with alternate portions of water and very dilute acetic acid, very little nickel dissolves in the solution and all of the lanthanum oxide is removed. The powder pattern of the resulting black product, for which d/n values are given in Table 4, is very nearly identical to that of $LaCoO_3$(13) prepared at the same temperature, 900°C. The nickel compound seems to be slightly less distorted from simple cubic than the cobalt one. $LaCoO_3$ is rhombohedral(13), with an interaxial angle of 90° 42'.

Lanthanum manganese oxide(8) was prepared by G. H. Jonker and J. H. van Santen at 1200°-1400°C, and found to have strong ferromagnetic properties due to variable valence of the manganese ion. Lanthanum manganese oxide has been made in this laboratory at 900°C. The compound prepared at 1200°-1400°C(8) was characterized as a deformed perowskite. That prepared here, at 900°C, in air, from lanthanum oxide and 80% manganous nitrate solution, can be indexed as simple cubic except for one weak line which does not appear to be associated with the pattern. Data are given in Table 5.

In the case of lanthanum iron oxide, reported as simple cubic by I. Naray-Szabo(9) and also by C. Guiot-Guillain(16), a series of well-defined, evenly spaced, additional lines was found in the product which was prepared in this laboratory at 900°C from lanthanum and ferric nitrates. These lines can be indexed on the basis of a doubled cubic cell. The material prepared by Guiot-Guillain was made at 1000°C, and that by Naray-Szabo at a yet higher temperature.

Table 5

X-ray Data Showing Lanthanum Manganese Oxide Prepared at 900°C, Indexed as a
Simple Perowskite

hkl	$h^2+k^2+l^2$	$I_{obs.}$	$d/n_{obs.}$	$d/n_{calc'd.}$
100	1	w+	3.90	3.886
110	2	s	2.76	2.748
111	3	m-	2.24	2.244
200	4	m	1.939	1.943
210	5	w	1.742	1.738
		w--	1.685	
211	6	m+	1.589	1.586
220	8	w+	1.373	1.374
300, 221	9	w-	1.296	1.295
310	10	w+	1.229	1.229
311	11	w-	1.172	1.172
222	12	w--	1.123	1.122
321	14	w+	1.042	1.039
411	18	w	0.916	0.916
420	20	w	0.867	0.871
332	22	w	0.829	0.829

Several methods had been used in an attempt to prepare a homogeneous product in the lanthanum-titanium(III)-oxygen system. The reducing agents employed were hydrogen gas, metallic lanthanum, metallic titanium, and the hydrides of lanthanum and titanium.

None of these methods resulted in a homogeneous product.

The method that ultimately produced a homogeneous sample in this system was prior reduction of titanium dioxide to titanium sesquioxide, which was used as a starting material with lanthanum oxide.

Titanium sesquioxide was prepared using the method of Friedel and Guerin(19). A stream of very dry deoxygenated hydrogen was saturated with titanium tetrachloride. This was passed over titanium dioxide, heated to 750°C, for forty-eight hours. Analyses showed the titanium sesquioxide prepared in this manner to be of 99+% purity.

The titanium tetrachloride used was not a commercial product, but was prepared immediately prior to being used by heating a very dry mixture of lampblack and titanium dioxide to a red heat while passing chlorine gas through the vycor tube containing the reactants(20).

All glass apparatus was used to prevent any contamination of the titanium tetrachloride.

The titanium tetrachloride collection bottle was immersed in an ice bath. The collected titanium tetrachloride was then distilled in an all glass distilling apparatus. The portion that was collected near 136°C was placed in a glass stoppered bottle and left overnight with a few copper turnings which were placed in the bottle. The almost clear titanium tetrachloride was then used immediately in the preparation of titanium sesquioxide.

Stoichiometric amounts of titanium sesquioxide and ignited lanthanum oxide according to the equation

$$Ti_2O_3 + La_2O_3 \longrightarrow 2LaTiO_3$$
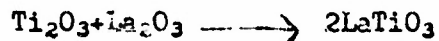
were ground thoroughly in an agate mortar and pressed into pellet form.

The sample was then heated in an evacuated sealed silica capsule at 1180°C for twenty-four hours. The capsule was removed from the furnace and cooled in air. The silica capsule was then broken and the pellet removed. The surface of the pellet was cleaned and the product examined. Visual examination showed this product to be heterogeneous. X-ray data showed the reactants to be present together with a new phase (or phases). The sample was then treated as before but at 1220°C.

This preparation was reground and reheated a second time for forty-eight hours.

The product obtained in this manner appeared homogeneous to the naked eye. The only phase that was observed in this product by microscopic investigation was a black, slightly iridescent one.

To be certain that all the titanium sesquioxide had been consumed in the reaction, a second preparation was made using a slight excess of lanthanum oxide. The same procedure was then repeated.

The product was removed from the silica capsule and ground in an agate mortar. The excess lanthanum oxide was removed by treatment with 2N hydrochloric acid. The black product was obtained in six successful experiments using titanium sesquioxide and lanthanum oxide as the starting materials.

The exact length of time required for the heating process at 1220°C might be very short, but two twenty-four hour periods were used as a precautionary measure.

Titanium Sesquioxide Analysis

It was found that the method of MacCardle and Scheffer(21) could be used in determining the composition of the lower oxide of titanium which was prepared following the procedure of Friedel and Guerin.

A weighed sample was placed in a platinum dish. A known amount of vanadium(V) solution was added to the sample. It is necessary that a sufficient quantity of vanadium(V) be added, not only to bring about complete oxidation of titanium(III, but also to leave enough vanadium(V) to make the final titration with Mohr's salt

solution feasible.

To this sample thirty ml of 9N sulfuric acid was added slowly. The mixture was heated cautiously to boiling. After allowing the sample to cool, ten ml of hydrofluoric acid was added, and the mixture heated until the sample dissolved. On cooling, the solution was placed in a beaker containing three hundred ml of water and ten ml of concentrated phosphoric acid.

Five drops of barium diphenylamine-p-sulfonate indicator was added and the solution was then titrated with standardized Mohr's salt solution to a blue green end point.

Equation:

$$Fe^{+2} + 2V^{+5} + Ti^{+3} \longrightarrow 2V^{+4} + Ti^{+4} + Fe^{+3}$$
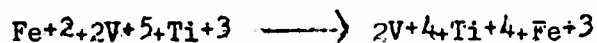
The per cent composition of titanium(III) was found to be 66.62 using this method of analysis, as compared to the theoretical value of 66.86.

Analysis of Black Product

A gravimetric analysis of the black product showed the total titanium content of the compound to be 19.75% and the lanthanum content to be 58.95%. Assuming the product to be $LaTiO_3$ the calculated per cent compositions of titanium and lanthanum are 20.40 and 59.16 respectively.

It can be seen that within experimental error the lanthanum to titanium ratio is one in the black product obtained.

Analysis of Black Product for Titanium(III) Content

A portion of the black product was ignited in air. The reaction that occurred was thought to be the following:

$$12LaTiO_3 + 3O_2 \xrightarrow{\triangle} 4La_2Ti_3O_9 + 2La_2O_3$$
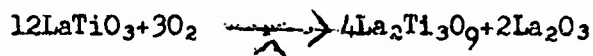
The increase in weight would indicate that all of the titanium in the black product is in the trivalent state.

This procedure showed the titanium(III) content to be 98.49% of the total titanium content.

A second method that was used to determine the valence of titanium was a

variation of the method of MacCardle and Scheffer(21). The sample was heated in
a platinum dish with fifty ml of 18N sulfuric acid and a known concentration of
vanadium(V) solution. The original procedure could not be followed as a pre-
cipitate was formed when hydrofluoric acid was added to the sample. It was
found that the remainder of the procedure of MacCardle and Scheffer could be
used and would give quantitative results if care was taken to avoid spattering
and air oxidation. The excess vanadium(V) was titrated with standardized Mohr's
salt solution.

Equation:

$$2V^{+5} + Fe^{+2} + Ti^{+3} \longrightarrow 2V^{+4} + Fe^{+3} + Ti^{+4}$$
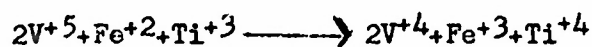
The experimental per cent composition of titanium(III) was found to be 20.57%.
This agrees very well with the total titanium content found theoretically to be
20.40%.

The evidence of all the analyses performed, indicate the product to be $LaTiO_3$.

The cell constant of the black product was calculated from x-ray diffraction
data and was found to be $3.92 \pm 0.01 Å$.

The density determined pycnometrically is 6.26 g/ml. The calculated density
for $LaTiO_3$ is 6.34 g/ml. This result shows that within experimental error each
unit cell contains one molecule of $LaTiO_3$.

I.5 The Employment of Mixed A-cations

To determine the effect of the presence of two A-cations on structure, a few
samples were prepared. X-ray data for them are tabulated in the Eleventh Quarterly
Report of this project. No analyses were made, and the formulae are based on the
ratios of the reactants.

The products were all deformed perowskite-like substances. They are listed
in the following table, Table 7, with cell sizes given on the basis of cubic
indices.

Table 6

X-ray Data for Lanthanum Titanium(III) Oxide

I	d/n	hkl
w+	4.19*	
w+	3.92	100
w	3.18*	
w+	2.99*	
s+	2.78	110
w	2.75*	
w---	2.65*	
w---	2.62*	
w---	2.37*	
w--	2.32*	
m+	2.27	**111**
w---	2.19*	
w	2.09*	
s	1.967	200
w	1.906*	
w--	1.842*	
w-	1.784*	
w	1.756	210
w	1.676*	
w-	1.645*	
s	1.603	211
w-	1.435*	
m	1.388	220
w--	1.309	300
m	1.241	310
w--	1.183	311
w	1.134	222
w	1.132*	
m-	1.040	321
w--	0.979	400
w--	0.948	322, 410
m+ diffuse	0.921	411
m- diffuse	0.873	331
m- diffuse	0.833	332

*-denotes lines attributed to oxidized product.

Table 7

Phase	Temperature of Preparation	Approximate Cell Size
$Ba_{0.5}Sr_{0.5}FeO_3$	900°C	3.91Å
$Ba_{0.5}La_{0.5}FeO_3$	900°C	3.94Å
#$Ba_{0.5}Ca_{0.5}FeO_3$	700°C	4.05Å
$Sr_{0.5}Ca_{0.5}FeO_3$	1000°C	3.85Å
$Sr_{0.33}La_{0.67}CrO_3$	900°C	3.87Å

#Product not entirely homogeneous

Among the products were several with quite simple structures. $Sr_{0.5}Ca_{0.5}FeO_3$ prepared from strontium nitrate, calcium carbonate and ferric oxide, has a simpler structure than the strontium-iron-oxygen phase prepared from nitrates at a corresponding temperature, and agreeing closely with that of the strontium iron oxide prepared at 900°C from strontium carbonate and ferric oxide (Table 3).

$Ba_{0.5}La_{0.5}FeO_3$ has an x-ray powder pattern containing fewer fine lines than the barium iron oxide prepared in this laboratory at 900°C, or the material designated $Ba_8Fe_8O_{22}$, produced at a slightly lower temperature by M. Erchak, I. Fankuchen, and R. Ward and considered to be a large, oxygen-deficient cube containing eight simple perowskite units defective in oxygen. $Sr_{0.33}La_{0.67}CrO_3$ seems to be a cubic, perowskite-like phase nearly identical in structure with $LaCrO_3$. If it is actually a single, stoichiometric phase, the valence of a third of the chromium should be four. Since the substance is nonmagnetic, the more probable explanation is that a small oxygen deficiency is present and the chromium is all in the trivalent state. This would seem, however, to be worth further investigation.

Table 8

Summary of Perowskite-like Oxides of the Alkaline Earths or Lanthanum and a Fourth Period Transition Metal

	La	Ba	Sr	Ca
Ti	P(11)	HP, OP, TP, P(3)	P(7)	OP(17)
V	DP		DP(2)*	DP(10)
Cr	P(9) or DP			
Mn	P or DP(8)	DP	DP?	P or DP(8)
Fe	LP or P(16,9)	HP, TP, (18) or LP(4)	P or DP(2)*	
Co	RP(13)	P(5) or HP?		
Ni	DP	HP(6)		

The formulae type suggested was $Sr_{0.67}M_{1.33}O_{2.67}$

Key:

P = essentially simple perowskite

HP = hexagonally deformed perowskite

OP = orthorhombic deformation of perowskite

TP = tetragonal deformation of perowskite

DP = deformed perowskite

LP = double celled perowskite

RP = rhombohedral deformation of perowskite

? = designation somewhat uncertain

II Defect Perowskite-like Compounds of the Tungsten Bronze Type

II.1 Strontium-Niobium-System

An investigation of a series of mixed oxides of strontium and niobium
(Table 9) has led to the discovery of a region of variable composition which is
characterized by direct relationships among the strontium content, the total
niobium content, and the apparent valence state of the niobium. The apparent
niobium valence state, which is regarded as an average of the proportions of
niobium in the pentavalent and the tetravalent states, decreases as the strontium
percentage increases and as the total niobium percentage decreases. These gradual
changes in composition are accompanied by gradual changes in some of the physical
properties, such as the color and the lattice dimensions.

Between the approximate composition limits $Sr_{0.70}NbO_3$ and $Sr_{0.93}NbO_3$, the
crystal structure is cubic or pseudo-cubic, the lattice constant increasing with
increasing strontium content from $3.981\pm0.001\overset{o}{A}$ to $4.024\pm0.001\overset{o}{A}$. A plot of the
lattice constants versus the strontium to total niobium ratio (Figure I) shows
that a nearly linear relationship exists between the composition and the lattice
dimensions. The scatter of the points about a straight line is rather wide and
it is not possible to detect any departure from Vegard's law.

The relative intensities of the x-ray diffraction lines of all the cubic
structure phases are comparable to those of perowskite, calcium titanate. The
unit cell of all such phases is probably a cubic cell with niobium at the corners
and oxygen at the edge centers with the ratio of one niobium to three oxygens
maintained, as in perowskite. The body-center positions are probably randomly
and incompletely occupied by strontium. It is not possible from any data obtained
for this system to state whether the niobium exists in both pentavalent and tetra-
valent forms or all in the pentavalent form with the extra electrons being assumed
by the lattice as a whole, as in a metal. Studies (22, 23) of the sodium-tungsten
bronze series showed that the only satisfactory explanation of the magnetic data
was the assumption that all the tungsten is hexavalent and that the sodium

Table 9

Summary of Data Obtained for Some Representative Products

Product Designation	Average Composition of Initial Mixture	Temp. of Prep'n. °C	Time of Prep'n. Hrs.	Composition of Product by Chemical Analysis	Product Color	X-Ray Diagram
A	$Sr_{0.50}NbO_3$	1200	14	--	White	Complex
B	$Sr_{0.65}NbO_3$	1100	2 x 24	$Sr_{0.585}NbO_{3.00}$	Black	Complex
C	$Sr_{0.70}NbO_3$	1100	2 x 24	$Sr_{0.675}NbO_{3.04}$	Blue-Black	Cubic + other lines $a_o = 3.981 \pm 0.001A$
D	$Sr_{0.75}NbO_3$	1050 / 1100	48 / 24	$Sr_{0.737}NbO_{3.06}$	Dark Blue	Cubic + few other lines $a_o = 3.985 \pm 0.001A$
E	$Sr_{0.80}NbO_3$	1050 / 1100	48 / 24	$Sr_{0.762}NbO_{3.04}$	Dark Blue	Cubic + few other lines $a_o = 3.993 + 0.001A$
F	$Sr_{0.85}NbO_3$	1050 / 1100	48 / 24	$Sr_{0.816}NbO_{3.06}$	Purple	Cubic + few other lines $a_o = 3.999 \pm 0.001A$
*G	$Sr_{0.80}NbO_3$	1150 / 1100	67 / 20	$Sr_{0.81}NbO_3$ **	Purple	Cubic + few other lines $a_o = 3.999 \pm 0.001A$
*H	$Sr_{0.85}NbO_3$	1025	20 + 18	$Sr_{0.820}NbO_{2.96}$	Purple	Cubic + few other lines $a_o = 4.009 \pm 0.001A$
*J	$Sr_{0.95}NbO_3$	1150	67	$Sr_{0.89}NbO_3$ **	Red	Cubic + few other lines $a_o = 4.015 \pm 0.001A$
*K	$Sr_{1.00}NbO_3$	1025	20 + 18	$Sr_{0.93}NbO_3$ **	Red + Trace Blue	Cubic + Tetragonal (?) $a_o = 4.024 \pm 0.001A$
*L	$Sr_{1.15}NbO_3$	1025 / 1125	48 / 42	----	Blue + Trace Red	Tetragonal (?)
P	$Sr_{1.20}NbO_3$	1200	48		Light Blue	Tetragonal (?)

*Tantalum Foil Used in Preparation **Composition Estimated From Lattice Constant

Lattice Constant Versus Strontium/Total Niobium Ratio
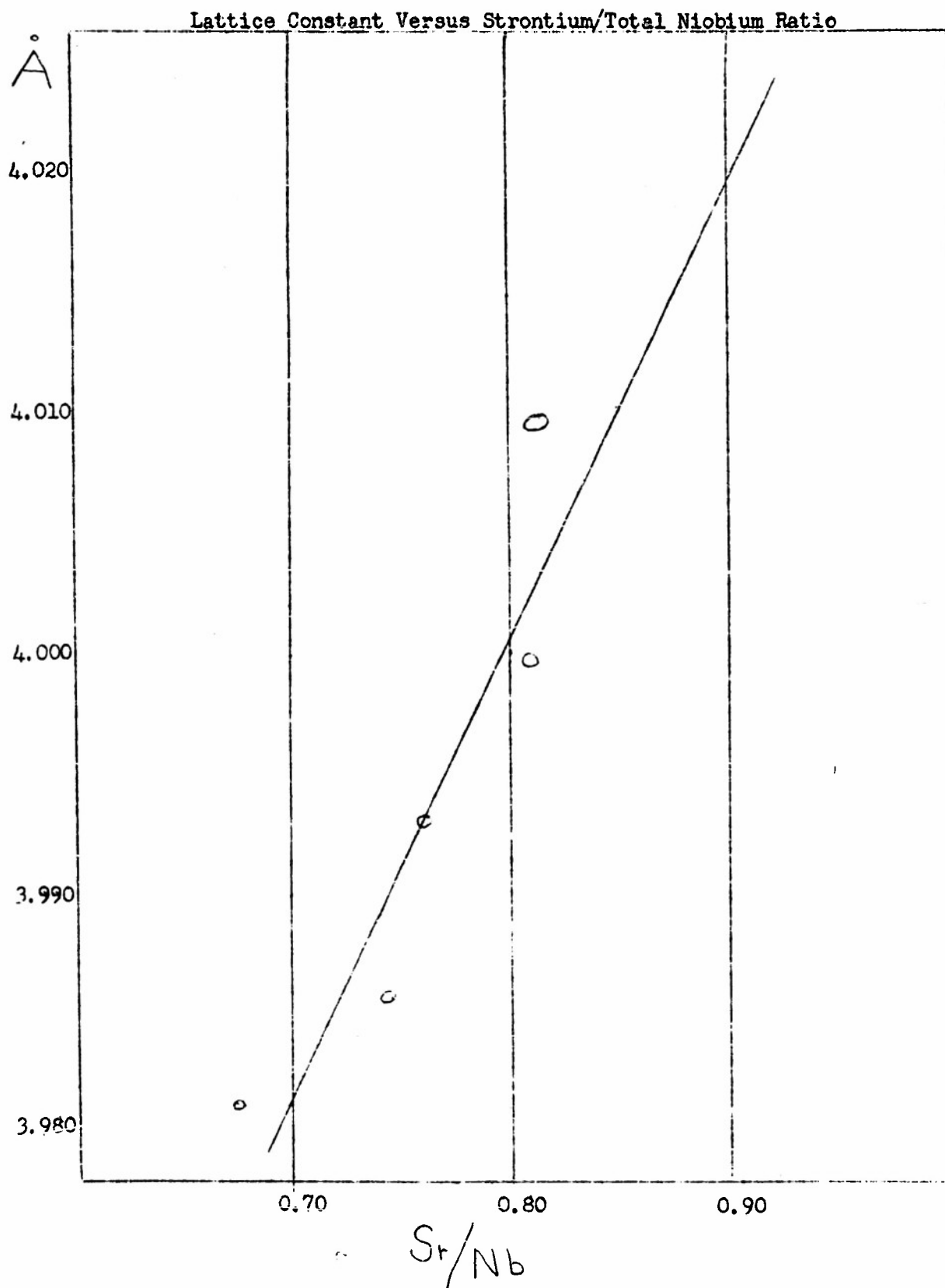
electrons are contributed to the conduction band of the crystal. The metallic conductivity of the sodium-tungsten bronzes is in agreement with this view. The strontium-niobium products have not been critically examined for paramagnetism, but no evidence of it was found on testing with a small magnet. Qualitative estimation of the conductivity of one sample with composition near $Sr_{0.80}NbO_3$ (estimated, not analyzed) showed a specific conducivity of the order of 0.6 $ohm^{-1}cm^{-1}$. These measurements were made on a powdered sample lightly compressed into a pellet with a small laboratory hand press.

Two essentially different methods were used in attempts to prepare the products of this series. The first of these was the heating of mixtures of strontium carbonate and niobium(V) oxide in a stream of hydrogen at $1150-1200°C$ for twenty-four to thirty-six hours. With the reactants in amounts such that the ratio of strontium to niobium was one, the result was a blue-black crystalline product which yielded a very complex x-ray powder diffraction pattern generally similar to that of Product B ($Sr_{0.59}NbO_{3.0}$). When a greater amount of strontium carbonate was used (Sr:Nb = 3:2), the product is a mixture of blue, white, purple, red, and brass-color phases. Regrinding and reheating this product in hydrogen yielded a uniform black sample with no traces of the colored phases. The second method was to wrap the pelleted reactants in tantalum foil and heat them in evacuated sealed silica capsules.

In view of the results of analyses of the colored products obtained by the first method, it appears that strontium in some form was volatilized from the samples during heating. This may have been one of the factors which made difficult the preparation of samples of high strontium content in the cubic structure range and which was partially brought under control by the use of tantalum foil. The analyses of the products all showed from 2% to 5% less strontium than was used in preparing the mixtures. Volatilization of strontium in some form may have been responsible in part for this discrepancy. The sodium-tungsten bronzes show a tendency to volatilize sodium metal(24) and this property may appear also

with the strontium-niobium series. If this be the case, the behavior of the samples described above would not be unexpected.

Product H ($Sr_{0.82}NbO_3$, Table 9) was the only one of the analyzed products which was prepared using tantalum foil and may contain additional niobium(IV) arising from reduction of a portion of the niobium(V) by the tantalum. It is also possible that the tantalum foil has acted to absorb any traces of oxygen which might have leaked into the capsules and partially oxidized the niobium samples. This might have been the case with the other products. The use of tantalum foil may also have influenced the volatilization of strontium during the evacuation and sealing of the capsules. Some measure of the effect of the tantalum foil can be seen by comparison of data from Product E with that of Product G and the data of Product F with that of Product H (Table 9), since these two pairs of products were prepared by heating mixtures of the same initial compositions, $Sr_{0.80}NbO_3$ and $Sr_{0.85}NbO_3$ respectively. Use of the foil appears, in effect, to result in a slight increase in the proportions of strontium and niobium(IV) and a slight decrease in the proportion of oxygen. In both cases the lattice constant is slightly larger when the foil was used and the intensities of the extra lines are somewhat reduced.

X-ray data are included in Tables 10-17, and these tables also include the data for three other products (Products G, J, and K) which were non-uniform and which were prepared using tantalum foil. If Vegard's law is assumed to hold here, the compositions of the phases of cubic structure present in these three products can be derived from Figure I as approximately $Sr_{0.80}NbO_3$, $Sr_{0.89}NbO_3$, and $Sr_{0.93}NbO_3$, using the respective lattice constants 3.999Å, 4.015Å, and 4.024Å. These samples were not analyzed because none was completely homogeneous under the microscope. The initial average compositions of the mixtures used in the preparation of these three products were respectively $Sr_{0.80}NbO_3$ $Sr_{0.95}NbO_3$, and $Sr_{1.00}NbO_3$. The phase of cubic structure in the first product (G) agrees in the lattice dimensions, and probably also in composition with Product F ($Sr_{0.81}NbO_3$)

which was prepared from a mixture with the average composition $Sr_{0.85}NbO_3$. The latter products (J and K) are probably contaminated with a phase richer in strontium than any of the cubic structure phases, since the x-ray diagram of these products shows additional weak lines coincident with those of a phase obtained by heating a mixture with the initial average composition $Sr_{1.15}NbO_{3.45}$. A preliminary study of the x-ray data of this last product indicated that the structure may have tetragonal symmetry.

In addition to the lines of the cubic structure, a number of other lines of extremely weak to weak intensity appear in the x-ray powder diffraction patterns of all products with compositions lying within the cubic range. The source of these cannot be definitely established. Many of the extra lines appear to be related in some manner to the cubic cell and also appear to shift with the lines of the cubic cell as the composition changes. Since only the weakest of the extra lines appear at the higher angle positions where the measured values are most accurate and the shift of the lines is most evident, these relationships are not at all certain.

The group of products with approximate compositions $Sr_{0.75}NbO_3$ (D), $Sr_{0.80}NbO_3$ (E), and $Sr_{0.85}NbO_3$ (F) and the group with the approximate compositions $Sr_{0.80}NbO_3$ (G), $Sr_{0.85}NbO_3$ (H), and $Sr_{0.95}NbO_3$ (J) show some consistency among the extra lines within each group, but this consistency does not extend from one group to the other. The letters D, E, F, G, H, and J designate products listed in Table 9. For the latter group of three products the samples were enclosed in tantalum foil envelopes during the preparation. This variation obviated somewhat the difficulty experienced in the preparation of samples relatively rich in niobium(IV), but could not be applied to the preparation of samples low in niobium(IV) because of attack on the tantalum.

The products from which all tabular data of this section are taken were prepared from mixtures of strontium oxide, niobium(IV) oxide, and niobium(V) oxide. Some preparations were also made using ignited strontium carbonate-niobium(V) oxide mixtures with niobium metal. X-ray diffraction patterns of products from both series of preparation mixtures agree closely in regard to the positions of the lines, but appreciable inconsistencies in the intensities of the lines not derived from the simple cubic unit cell were evident.

The diffraction lines unaccounted for on the basis of the simple cubic cell must arise either from the presence of impurities or from the existence of a non-cubic atomic arrangement within the crystal. None of the lines could be attributed to strontium oxide, hydroxide or carbonate, to any niobium oxide as reported by Brauer (25) or to the compound $Sr_{0.5}NbO_3$. In view of the poor agreement between the diagrams of the various products in regard to these unassigned weaker lines, it is very unlikely that they arise entirely from any single impurity in the samples or from impurities in the materials used in the preparations, since these were taken from the same container in nearly every case.

Some success was attained in attempts to index the diagrams of products with the approximate compositions $Sr_{0.68}NbO_3$, $Sr_{0.80}NbO_3$ and $Sr_{0.89}NbO_3$ on the basis of a tetragonal cell with a. four times and c. twice the length of the cell edge of the simple cubic cell. The large size of this cell, however, renders the agreement between the calculated and measured values rather questionable.

Any complex or multiple cell derived which yields a satisfactory index of the diagrams must maintain the strontium and niobium atoms in the same relative positions as in the cubic cell since none of the lines of the cubic phase are shifted or split. Any factors, therefore, which cause the symmetry to deviate from cubic must be associated with the oxygen atoms or with a non-random arrangement of the strontium or of tantalum atoms which are present as impurity.

The limits of the region of variable composition were not definitely established. The product of cubic structure with the highest strontium content, designated as Product K, appears to contain a small amount of a phase which was prepared from a mixture of the initial average composition $Sr_{1.15}NbO_{3.45}$. The cubic phase of Product K was estimated to have a composition near $Sr_{0.93}NbO_3$. Only one product was prepared between the lower limit of the cubic structure range, $Sr_{0.70}NbO_3$, and the compound $Sr_{0.5}NbO_3$. This product was obtained from a preparation mixture with an initial average composition of $Sr_{0.65}NbO_3$ and was analyzed as $Sr_{0.59}NbO_{3.0}$. The x-ray powder diffraction pattern of this product (Product B) is rather complex and shows a large number of strong lines. The lines of a cubic cell with a lattice constant of about $3.981\overset{o}{A}$ can be found within this pattern. This may indicate the presence of a cubic phase in this product, in addition to a complex structure phase. The possibility still exists that the product belongs to the variable composition range but possesses a perowskite-like structure, distorted from cubic symmetry.

Table 10

Lines of X-ray Powder Diffraction Pattern of Product C
Assigned to a Cubic Cell $a_o = 3.981 \pm 0.001$ Å

Cu Kα Radiation, 30 kva, 17 ma , 50 Hrs., Camera Radius 107.6 mm

Estimated Intensity Observed	$h^2+k^2+l^2$	d (Å)	
		Observed	Calculated
s-	1	4.00	3.981
vs	2	2.815	2.815
w	3	2.30₃	2.298
s+	4	1.993	1.990
m	5	1.783	1.780
s+	6	1.627	1.625
s	8	1.410	1.407
w+	9	1.329	1.327
s-	10	1.261	1.259
--	11	----	1.200
m	12	1.150	1.149
vw+	13	1.105	1.104
s	14	1.066	1.064
m-	16	0.9964	0.9953
w+	17	0.9664	0.9656
s-	18	0.9391	0.9383
--	19	----	0.9133
s-	20	0.8906	0.8902
w	21	0.8692	0.8687
m	22	0.8490	0.8488
s-	24	0.8127	0.8126
w-	25	0.7964	0.7962
s+	26	0.7808	0.7808

Table 11

Lines of X-ray Powder Diffraction Pattern of Product D
Assigned to a Cubic Cell $a_o=3.985\pm0.001$Å.
Cu K α Radiation, 30 kva, 17 ma , 56 Hrs., Camera Radius 107.6 mm

Estimated Intensity Observed	$h^2+k^2+l^2$	d (Å)	
		Observed	Calculated
m+	1	3.99	3.985
vs	2	2.82	2.818
w-	3	2.30	2.301
s+	4	1.993	1.993
m-	5	1.784	1.782
s+	6	1.628	1.627
s	8	1.409	1.409
w+	9	1.329	1.328
s	10	1.260	1.260
vvw-	11	1.201	1.202
m	12	1.151	1.150
vw+	13	1.106	1.105
s	14	1.065	1.065
m-	16	0.997_8	0.9963
w	17	0.967_8	0.9665
s-	18	0.940_3	0.9393
--	19	----	0.9142
s-	20	0.8920	0.8911
w	21	0.8704	0.8696
m+	22	0.8502	0.8496
s-	24	0.8139	0.8134
w-	25	0.7974	0.7970
vs-	26	0.7818	0.7815

D_4^{31} = 5.21 gms /cc   (Pycnometric)
Density calculated for $Sr_{0.373}NbO_3$=5.39gm /cc

Table 12
Lines of X-ray Powder Diffraction Pattern of Product E
Assigned to a Cubic Cell a$_0$=3.993+0.001A.
Cu Kα Radiation, 35 kva, 17 ma , 48 Hrs., Camera Radius 107.6 mm.

Estimated Intensity Observed	$h^2+k^2+l^2$	d (Å)	
		Observed	Calculated
m+	1	4.00	3.993
vs	2	2.83$_3$	2.823
w	3	2.31$_3$	2.305
s+	4	2.00$_2$	1.996
m-	5	1.789	1.786
s+	6	1.634	1.630
s-	8	1.415	1.412
w	9	1.334	1.331
s-	10	1.265	1.263
--	11	----	1.204
m-	12	1.155	1.153
w-	13	1.109	1.107
s	14	1.067	1.067
m-	16	0.998$_7$	0.9982
w	17	0.969$_0$	0.9685
s	18	0.941$_3$	0.9412
--	19	----	0.9161
s	20	0.8929	0.8929
w	21	0.8716	0.8714
m+	22	0.8514	0.8513
s-	24	0.8151	0.8151
vw	25	0.7985	0.7986
vs	26	0.7829	0.7831

Table 13

Lines of X-ray Powder Diffraction Pattern of Product F
Assigned to a Cubic Cell $a_c = 3.999 \pm 0.001$Å.

Cu K_α Radiation, 35 kva, 17 ma., 48 Hrs., Camera Radius 107.6 mm.

Estimated Intensity Observed	$h^2 + k^2 + l^2$	d (Å)	
		Observed	Calculated
m	1	4.01	3.999
vs	2	2.829	2.828
w-	3	2.31₃	2.309
s+	4	2.00₄	2.000
w+	5	1.792	1.788
s	6	1.635	1.633
m+	8	1.416	1.414
w	9	1.336	1.333
m	10	1.26₇	1.265
vvw-	11	1.206	1.206
m-	12	1.156	1.154
vvw+	13	1.111	1.109
s	14	1.070	1.069
w	16	1.000	0.999₈
vw	17	0.970₀	0.969₉
m+	18	0.942₇	0.942₆
--	19	----	0.917₅
m+	20	0.8944	0.8942
vw	21	0.8726	0.8727
m	22	0.8528	0.8526
m+	24	0.8165	0.8163
vw-	25	0.7998	0.7998
s	26	0.7844	0.7843

Table 14

Lines of X-ray Powder Diffraction Pattern of Product G
Assigned to a Cubic Cell $a_o = 3.999 \pm 0.001 Å$.
Cu $K\alpha$ Radiation, 40 kva, 17 ma , 60 Hrs., Camera Radius 107.6 mm

Estimated Intensity Observed	$h^2+k^2+l^2$	d (Å)	
		Observed	Calculated
m	1	4.02	3.999
vs	2	2.82_7	2.828
w-	3	2.31_3	2.309
s	4	2.00_3	2.000
m-	5	1.791	1.788
s	6	1.634	1.633
m+	8	1.416	1.414
vw+	9	1.335	1.333
m	10	1.267	1.265
--	11	----	1.206
w+	12	1.156	1.154
vw-	13	1.111	1.109
m+	14	1.070	1.069
w+	16	1.001	0.999_8
vw+	17	0.971_1	0.969_9
m+	18	0.943_4	0.942_6
--	19	----	0.917_5
m+	20	0.8951	0.8942
w-	21	0.8733	0.8727
m	22	0.8533	0.8526
m+	24	0.8168	0.8163
w-	25	0.8002	0.7998
s	26	0.7845	0.7843

$D_4^{31} = 5.43$ gms /cc (Pycnometric)
Density calculated for $Sr_{0.82}NbO_3 = 5.48$ gms /cc

Table 15

Lines of X-ray Powder Diffraction Pattern of Product H
Assigned to a Cubic Cell $a_o = 4.009 \pm 0.001Å$.
Cu K_α Radiation, 30 kva, 17 ma , 60 Hrs., Camera Radius 107.6 mm

Estimated Intensity Observed	$h^2+k^2+l^2$	d (Å) Observed	d (Å) Calculated
m-	1	4.04	4.009
vs	2	2.85_2	2.835
w	3	2.32_9	2.315
s+	4	2.01_7	2.005
w+	5	1.801	1.793
s+	6	1.642	1.637
s	8	1.422	1.417
vw+	9	1.340	1.336
s	10	1.271	1.268
--	11	----	1.209
m-	12	1.160	1.157
vvw+	13	1.115	1.112
s	14	1.074	1.071
w+	16	1.003	1.002
vw-	17	0.973_1	0.9723
s	18	0.945_5	0.9449
--	19	----	0.9197
s-	20	0.8970	0.8965
vw-	21	0.8753	0.8748
m+	22	0.8550	0.8547
s-	24	0.8186	0.8183
vvw+	25	0.8019	0.8018
s+	26	0.7864	0.7862

Table 16

Lines of X-ray Powder Diffraction Pattern of Product J
Assigned to a Cubic Cell $a_0 = 4.015 \pm 0.001$ Å.
Cu K_α Radiation, 30 kva, 17 ma , 68 Hrs., Camera Radius 107.6 mm

Estimated Intensity Observed	$h^2+k^2+l^2$	d (Å)	
		Observed	Calculated
m	1	4.03	4.015
vs+	2	2.84_9	2.839
w	3	2.32_4	2.318
vs	4	2.01_2	2.007
m-	5	1.800	1.796
vs	6	1.642	1.639
s+	8	1.422	1.420
w-	9	1.340	1.338
s+	10	1.271	1.270
--	11	----	1.211
m	12	1.161	1.159
vw	13	1.115	1.114
s+	14	1.075	1.073
m	16	1.005	1.004
w-	17	0.975_0	0.973_0
s	18	0.947_3	0.9463
--	19	----	0.9211
s-	20	0.8985	0.8978
w-	21	0.8768	0.8762
m+	22	0.8566	0.8560
s-	24	0.8200	0.8195
vw	25	0.8034	0.8030
vs	26	0.7877	0.7874

Table 17

Lines of X-ray Powder Diffraction Pattern of Product K
Assigned to a Cubic Cell a_o=4.024±0.001A.
Cu K_α Radiation, 35 kva, 17 ma., 16 Hrs., Camera Radius 57.? mm.

Estimated Intensity Observed	$h^2+k^2+l^2$	d (Å)	
		Observed	Calculated
m-	1	4.02	4.024
vs	2	2.84₅	2.845
w+	3	2.32₄	2.323
s+	4	2.01₂	2.012
w+	5	1.801	1.800
s+	6	1.643	1.643
s	8	1.424	1.423
w-	9	1.342	1.341
s-	10	1.272	1.272
vvw-	11	1.215	1.213
m	12	1.162	1.162
--	13	----	1.116
s	14	1.078	1.075
w+	16	1.007	1.006
vw	17	0.975₁	0.9760
m+	18	0.948₀	0.9485
--	19	----	0.9232
m	20	0.8996	0.8998
vw-	21	0.8780	0.8781
m-	22	0.8577	0.8579
m	24	0.8213	0.8214
vvw	25	0.8044	0.8048
s+	26	0.7892	0.7892

II. 2 Sodium-Tungsten-Molybdenum-Oxygen-System

During the past year work has been centered on the analysis of the black sodium tungsten-molybdenum oxides whose preparation and properties have been described in previous reports(26,27,28). The results of the chemical analysis of representative samples and a brief description of some of their physical and chemical properties are given here.

The black oxides are best prepared by the electrolytic reduction of fused mixtures of sodium tungstate or molybdate, tungsten(VI) oxide, and molybdenum(VI) oxide. The details of this and other preparations are given in the Sixth and Ninth Quarterly Reports(26,28) of this project.

The range of formation of black products, based on the mole ratio of starting materials, is $Na/M=0.4-0.8$ (i.e. sodium to tungsten plus molybdenum equals 0.4 to 0.8) and $W/Mo=0.17-5.0$ (tungsten to molybdenum equals 0.17 to 5.0). X-ray powder diffraction patterns show that this range may be subdivided into three smaller ranges. A very complicated pattern(I) is obtained for products having starting ratios of $Na/M=0.4-0.5$ and $W/Mo=1.5$. This pattern does not correspond to that of any known compound of tungsten or molybdenum. Pattern (II), obtained in the range $Na/M=0.5-0.8$ and $W/Mo=0.17-5.0$, is similar to but not identical with (I). The powder pattern obtained at $Na/M=0.40$ and $W/Mo=0.67$ is that of an expanded WO_3 lattice. All powder patterns are very complex and have not been indexed. A summary of the methods of preparation and the x-ray pattern types of the products is given in Table 18. The powder pattern data appear in Tables 21, 22, and 23.

The black products are generally inert to the action of acids and are insoluble in hot alkali and carbonate solution of concentration less than 1N. They are brought into solution by fusion with alkali carbonate or persulfate. The attack by bases is more noticable for products with low W/Mo ratios. The best yields were obtained at $Na/M=0.6$, $W/Mo=1.0-2.0$. The products of decomposition are tungsten(VI) oxides, and sodium tungstate and molybdate. All black products are hard and brittle, with hardness apparently decreasing as the ratio of W/Mo is

lowered. None of the products shows appreciable electrical conductivity. All products are highly crystalline and quite lustrous.

Chemical analysis of four representative samples, having x-ray pattern(II), showed a wide range of interchange between tungsten and molybdenum with the amount of tungsten increasing as the starting ratio of W/Mo is increased. Analytical data justify the general emperical formula $Na_{0.31-0.35}(W,Mo)O_3$. The results of the analysis and the emperical formulae assigned are given in Tables 19 and 20. The structure type in each of these cases is that designated as (II).

Table 18

Summary of Preparation

Moles of Starting Materials

Na_2WO_4	WO_3	MoO_3	Na/M	W/Mo	X-ray type
0.02	--	0.02	1	1	no black product
0.01	0.02	0.02	0.4	1.5	I
0.015	0.015	0.03	0.5	1.5	I
0.01 *	--	0.05	0.57	0.17	II
0.075 †	0.0025	0.0325	0.64	0.24	II
0.0175	--	0.0525	0.50	0.33	I1
0.01	--	0.025	0.57	0.40	II
0.01	--	0.02	0.67	0.50	II
0.020	0.0022	0.044	0.70	0.50	II
0.01	0.01	0.02	0.50	1.0	II
0.015	0.015	0.02	0.60	1.0	II
0.015	0.015	0.02	0.60	1.5	II
0.022	0.020	0.021	0.70	2.0	II
0.010	0.010	0.008	0.71	2.5	II
0.022	0.02525	0.01575	0.70	3.0	II
0.014	0.018	0.008	0.70	4.0	II
0.010	0.015	0.005	0.67	5.0	II
0.020	0.005	0.025	0.80	1.0	II
0.020	0.01	0.20	0.80	1.5	II
0.01	0.01	0.03	0.40	0.67	III

* 0.01 moles of Na_2MoO_4 used in addition.

† 0.009 moles of Na_2MoO_4 used in addition.

Table 19

Analysis of Representative Products Obtained in Na-W-Mo-O System.

Starting Mole Ratios

Na/M	W/Mo	% Na	% W	% Mo	% O
0.5	0.33	3.56	54.80	17.62	24.02
0.7	0.5	3.75	61.94	11.95	22.36
0.6	1.5	3.58	67.20	7.98	21.24
0.7	3.0	3.59	70.77	4.12	21.52

Table 20

Emperical Formulas Based on Results Given in Table 19.

Starting Mole Ratios

Na/M	W/Mo	Formulae Assigned
0.5	0.33	$Na_{0.31}W_{0.60}Mo_{0.37}O_3$
0.7	0.50	$Na_{0.35}W_{0.72}Mo_{0.27}O_3$
0.6	1.5	$Na_{0.35}W_{0.82}Mo_{0.19}O_3$
0.7	3.0	$Na_{0.35}W_{0.87}Mo_{0.10}O_3$

It will be noted that some of the values given in Table 19 differ from those given in a previous report(29). This may be due to the formation of molybdenum(IV) oxide as a side product in the electrolytic preparation. It was found that the percentage of molybdenum in a product electrolyzed for 1 hour was 7.98% while the percentage of molybdenum in another product having the same starting mole ratios electrolyzed for 2 hours was 6.37%.

Table 21

X-ray Powder Pattern Type I

I	d/n	I	d/n
m	4.65	vvw	1.352
m	3.87	vw	1.313
vs	3.66	vvw	1.297
vvw	3.50	vvw (B)	1.250
vs	3.14	vvw	1.229
m	2.68	vw	1.194
m	2.62	vvw	1.169
m	2.51	vvw	1.144
m	2.47	vvw	1.128
vvw	2.36		
w	2.17		
w	2.045		
vvw	2.021		
vvw	1.974		
vw	1.924		
vw	1.865		
s	1.815		
vvw	1.716		
w (B)	1.646		
w	1.577		
vvw (?)	1.557		
vw	1.524		
vw	1.490		
vvw	1.459		
vvw	1.362		

(lines not read further)

Note: (B) = broad

(?) = line reading uncertain

Table 22

X-ray Powder Diffraction Pattern Type II

(lines present in Pattern I are underlined, those possibly present ----)

I	d/n	I	d/n	I	d/n
m	5.14	vvw	1.518	vw	1.032
s	4.65	vw	1.429	w	1.019
vw	4.26	w	1.472	w	1.010
w	3.83	w (B)	1.453	w	1.003
vs	3.69	vw (B)	1.430	vw	0.977
w	3.48	w	1.369	vw	0.962
vs	3.14	w (B)	1.348	w	0.952
w	3.03	vvw	1.328	vvw	0.942
m	2.76	w	1.308	vw	0.929
ms	2.52	vw	1.297	vw	0.913
ms	2.45	vvw	1.282	w	0.907
w	2.32	w	1.264	w	0.897
vvw	2.23	vw	1.239	vvw	0.890
m	2.11	w	1.222 X	vw	0.884
m	2.038	vw	1.206	vw	0.877
w	1.905	ms	1.191	m	0.871
s	1.815	vw	1.168	vw	0.863
vvw	1.778	vw	1.150	w	0.850
vw	1.774	ms	1.140	vw	0.836
vw	1.723	vw	1.131	w	0.830
vvw	1.682	vvw	1.105		
vvw	1.664	vvw	1.093		
m	1.631	vvw	1.081		
m	1.617	vw	1.070		
m	1.575	w	1.052		

X All products listed as having pattern II show all the listed lines to w 1.222. Past this point some products give patterns in which some of the vvw lines appear to be absent or shifted slightly.

Table 23

Comparison of Pattern Type III and That of Tungsten(VI) Oxide

Type III		WO$_3$		Type III		WO$_3$	
I	d/n	I	d/n	I	d/n	I	d/n
w	4.11			m	1.664	m	1.666
s	3.87	vvs	3.79	vw	1.598	vvw	1.583
s	3.71	s	3.63	vw	1.557	vw	1.557
w	3.35	m	3.34	w (B)	1.525	m (B)	1.533
m	3.13	m	3.09	w	1.493	m (B)	1.495
w	2.98			vw	1.466	w	1.466
vw	2.88			vw	1.411	w	1.407
vw	2.79	vvw	2.81	w	1.389	w	1.382
s	2.68	s	2.68	vw (B)	1.346	w	1.335
m	2.63	s	2.62	vw	1.313	m	1.308
w	2.54	w	2.52	vw	1.287	vvw	1.299
		vvw (B)	2.40	vvw	1.283	w	1.284
vvw (B)	2.27	vvw (B)	2.25	m (B)	1.252	w	1.257
m	2.16	m	2.15	vw	1.229	s	1.237
vvw	2.090	vw	2.097			w	1.215
		w	2.034	vvw	1.186	vw	1.195
m	2.013	w	2.006	vw	1.171	m	1.175
		w	1.967			w	1.162
w	1.931	m	1.921	w	1.156	m	1.154
w	1.881	m	1.877			w	1.141
m	1.817	m	1.822	w	1.130	m	1.127
		m	1.801	vw	1.115	m	1.112
vvw	1.770	vvw	1.752	vvw	1.100	w	1.101
w	1.720	m	1.711	vw (B)	1.089	vw	1.082
		m	1.692	vw (B)	1.065	w	1.070

III. Exploitation of New Structural Types

At present three new structural types are being studied. The results of preliminary investigations appear under this heading.

III.1 Phases With Possible Defect Fluorite Structure

Cerium zirconium oxide, $Ce_2Zr_2O_7(30)$, has been prepared and showed to form a defect fluorite type structure. In order to index all of the lines of the x-ray diffraction pattern of this phase, the dimensions of the unit cell had to be doubled. This larger unit cell, which still retains its face-centered cubic arrangement must therefore have an ordered deficiency in oxygen.

Lanthanum zirconium oxide, $La_2Zr_2O_7(30,31)$ is structurally very similar to $Ce_2Zr_2O_7$.

The general formula for this type product would be $M_2^{III}M_2^{IV}O_7$.

In the Eleventh Quarterly Report of this project(32), several unsuccessful substitutions were made for cerium and zirconium.

The next group of substitutions that were made for the M^{IV} cation were uranium, cerium and thorium. The starting materials employed throughout these investigations were uranyl nitrate, cerium(III) oxalate and thorium nitrate, respectively.

In the first group of experiments lanthanum was used as the M^{III} cation.

In this and in all further work reported here, the following procedure was maintained.

Stoichiometric quantities of reactants, as governed by the general formula $M_2^{III}M_2^{IV}O_7$ were thoroughly ground in an agate mortar. The sample was then heated slowly to 900°C in air in zirconium silicate combustion boats. After the gaseous products were evolved completely, the preparations were heated at 1200°C in air for twenty-four hours. The products were then cooled and prepared for x-ray analysis.

The lanthanum-thorium, lanthanum-cerium, and lanthanum-uranium products exhibit a face-centered cubic arrangement.

The following reactants were then substituted for the M^{III} cation:

$$MnO_2 \quad (or \ Mn(NO_3)_2); \ Y_2O_3; \ Cr(NO_3)_3$$

$$Fe_2O_3 \qquad\qquad\qquad CoCO_3$$
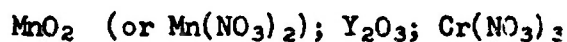
In all of the products except three, there were present phases that could be indexed as face-centered cubic. The exceptions were the phases obtained using uranium as M^{IV} and cobalt, chromium, and iron as M^{III}.

In these instances the structures of the products obtained have not been determined.

The extent of similarity of the phases that were obtained in these trial substitutions to the phase observed in the product $Ce_2Zr_2O_7$ has not been ascertained. The x-ray patterns of these new phases have not been minutely examined for the presence of weak lines, which might mean that the unit cell reported in Table 24 should be doubled. This work is still in progress as are new substitutions for M^{III} and M^{IV} cations.

Table 24

Data Obtained by Substitutions in the System $Ce_2Zr_2O_7$

Expected Product	Basic Structure	Unit Cell Size ± 0.02Å
$La_2Th_2O_7$	F.C.C.	5.64Å
$Fe_2Th_2O_7$	F.C.C.	5.60Å
$Cr_2Th_2O_7$	F.C.C.	5.58Å
$Co_2Th_2O_7$	F.C.C.	5.59Å
$Mn_2Th_2O_7$	F.C.C.	5.59Å
$Y_2Th_2O_7$	F.C.C.	5.55Å
$La_2Ce_2O_7$	F.C.C.	5.56Å
$Fe_2Ce_2O_7$	F.C.C.	5.41Å
$Cr_2Ce_2O_7$	F.C.C.	5.42Å
$Co_2Ce_2O_7$	F.C.C.	5.44Å
$Mn_2Ce_2O_7$	F.C.C.	5.41Å
$Y_2Ce_2O_7$	F.C.C.	5.47Å
$La_2U_2O_7$	F.C.C.	5.49Å
$Fe_2U_2O_7$	?	
$Cr_2U_2O_7$	?	
$Co_2U_2O_7$	?	
$Mn_2U_2O_7$	F.C.C.	5.28Å
$Y_2U_2O_7$	F.C.C.	5.36Å

F.C.C. = face-centered cubic   ? = not known

Comments: The formula for the expected product is based on the quantities of the starting materials that were used. The structures are based on the more intense lines of the x-ray patterns.

III.2 Phases of the General Type $M_2Cr_6O_{16}$

A preliminary investigation of alkali metal compounds of the type $M_2Cr_6O_{16}$ has been started and isomorphous substitution attempted.

A series of compounds of the type $M_2Cr_6O_{16}$ (M= Li, Na, K, Rb, Cs) has been synthesized by heating the appropriate alkali metal dichromate with chromium trioxide at 350°C(33).

$$M_2Cr_2O_7 + 4CrO_3 = M_2Cr_6O_{16} + 3/2O_2$$

All of the black products, save the lithium compound which is orthorhombic, have monoclinic symmetry and are believed to contain two trivalent and four hexavalent chromium atoms in the unit cell. As a starting point the lithium, sodium and potassium compounds have been prepared and their x-ray diffraction patterns obtained.

Several methods of producing isomorphous substitution in the formula $M_2^{I}Cr_2^{III}Cr_4^{VI}O_{16}$ have been attempted. Hexavalent molybdenum, in the form of sodium molybdate dihydrate, was mixed with chromium trioxide in a molar ratio of 1 to 2 and heated for two hours at 350°C. The materials which did not undergo reaction were extracted with water. This yielded a product which had an x-ray pattern remarkably similar to that of $Na_2Cr_6O_{16}$ and gave qualitative tests for sodium, chromium, and molybdenum.

When hexavalent tungsten, in the form of sodium tungstate dihydrate, was mixed with chromium trioxide the water insoluble products appeared to be a heterogeneous mixture which showed only indistinct diffraction patterns.

Substitution for the trivalent chromium has also been attempted. $KFeCr_2O_8$ has been prepared by the method of Weinland and Mergenthaler(34) and the substance annealed at 350°C. This type of substitution has also been attempted by a direct reaction between ferric nitrate and potassium dichromate in the solid state, at 350°C. Both substances give rise to the same product, as shown by identical

x-ray diffraction patterns. The patterns are remarkably similar to those of ferric oxide but the products gave qualitative tests for chromium, iron and potassium. The possibility of solid solutions of chromic oxide in ferric oxide has been considered but the x-ray diffraction patterns do not shift over a range of compositions from Fe:Cr=1:1, 1:2 and 1:5. Attempts to prepare a molybdenum compound with a similar pattern have thus far failed.

Other substitutions are under consideration.

III.3 Preliminary Studies in the System Barium-Platinum-Oxygen

In a thesis by I. Hegyi(35) on the preparation of barium-platinum-oxygen compounds, a product thought to be Ba_2PtO_x was discussed. It was obtained by the solid phase reaction between platinic oxide and barium peroxide in the molar ratio of 1:2 at 1000°C. This sample gave inconsistent analyses, so a definite formula could not be deduced.

Similar samples have been prepared using starting ratios of barium to platinum of three or greater. The resulting products are homogeneous. X-ray diffraction patterns indicate that the products are the same in all cases, and none of the lines can be attributed to impurities.

This preparation will be analyzed in an attempt to assign a definite formula. If this meets with success, structural investigations of this system will be initiated.

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